THE RELATIONSHIP BETWEEN SOIL pH AND BASE-SATURATION PERCENTAGE FOR SURFACE AND SUBSOIL HORIZONS OF SELECTED MOLLISOLS, ALFISOLS, AND ULTISOLS IN OHIO[1, 2]

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ABSTRACT

In the 7th Approximation soil classification system, base-saturation percentage is used as a definitive criterion in separating Alfisols (Gray-Brown Podzolics) from Ultisols (Red-Yellow Podzolics) and Umbric epipedons (acidic, dark-colored surface horizons) from Mollic epipedons (other dark-colored surface horizons). Ohio soil scientists are currently using field-determined pH to estimate base-saturation percentage when laboratory data are unavailable. To test the reliability of this estimation, soil pH was measured in water and in KCl for three horizons (Ap, B1, and B2) for 64 soils comprising three soil orders in Ohio—Mollisols (Humic Gleys), Alfisols, and Ultisols. Linear regression analysis was used to correlate pH in KCl with pH in water, and base-saturation percentage with both pH in water and KCl.

Soil pH in KCl was highly correlated (r=0.897 to 0.984) with pH in water, and pH in KCl can be accurately predicted from simple regression equations. It is about one unit lower than the pH value in water. There is a closer relationship between base-saturation percentage and pH measure in water (r=0.668 to 0.928) versus that measured in KCl. Soil pH measured in water correlates more closely with base-saturation percentage for Ap horizons (r=.838 to .928) than for subsoil horizons (r=.668 to .801). For all horizons of Mollisols, and Ap horizons of both Alfisols and Ultisols, relatively smaller amounts of H^+ are released from the exchange complex by addiction of KCl to the soil suspension.

INTRODUCTION

Agronomically, soil pH is an important soil property which affects nutrient availability, lime requirement, and soil productivity. This property is defined as the negative logarithm of the hydrogen-ion activity and in soils is frequently referred to as active acidity. From a soil-engineering point of view, pH affects the corrosiveness of soils to concrete and metal implacements, as well as soil stability. Geologists and pedologists have long used pH as an index of soil weathering and mineral transformations. Because of its importance and the number of co-varying properties related to it, pH has historically been considered an important criterion for soil classification.

In the chemical characterization of a soil, pH is one of the properties measured routinely both in the field and laboratory. It is measured in a variety of ways.

[1]Contribution of the Agronomy Department, Ohio Agricultural Research and Development Center. Project No. State 106. Journal Paper No. 18-70. Columbus, Ohio.
[2]Manuscript received August 10, 1969.

Peech *et al.* (1947) and Reed and Cummings (1945) have suggested measuring pH in a 1:1 soil-to-water suspension. However, Schofield and Taylor (1955) and Puri and Asghar (1938) recommend that pH be measured in a salt solution. A salt solution is used to mask the variability in the salt content of soils, to maintain the soil in a flocculated condition, and to decrease the junction-potential effect (Coleman *et al.*, 1950; Jenny *et al.*, 1950).

With the implementation of the new Comprehensive Soil Classification System (7th Approximation) by the Soil Survey Staff (1960), greater attention and emphasis have been given to the base saturation of a soil to separate classes at high categorical levels (orders and subgroups). Dark-colored, relatively thick surface horizons with base saturations greater than 50% (called *mollic* epipedons) characterize the Mollisols and Mollic intergrades, those soils formerly classed as Brunizems (Prairie) and Humic Gleys of the 1938 Soil Classification scheme presented by Baldwin *et al.* (1938). Similar dark-colored surface horizons, but with base saturations less than 50%, are called *umbric* epipedons, and characterize more acid soils differentiated from the Mollisol order. Alfisols (formerly classed as Gray-Brown Podzolics) are differentiated from Ultisols (Red-Yellow Podzolics) by their higher base saturation at a specified depth in or below the argillic horizon. An argillic horizon is defined as a mineral-soil horizon that is characterized by illuvial (translocated) accumulation of layer-lattice silicate clays. Ultisols have base saturations at a depth of 50 inches below the top of the argillic horizon of less than 35%, while in Alfisols it is above 35%. Currently, this separation is made in the field by soil scientists using field estimates of pH to infer base saturation. Geographically in Ohio, Ultisols occur principally in the unglaciated region (southeastern third of the state), Mollisols are confined primarily to the strongly calcareous till region of western Ohio, and Alfisols are extensive throughout the entire state.

Numerous attempts have been made to correlate base-saturation percentage with pH in salt or water suspensions (Keeney and Corey, 1963; Mehlich, 1941, 1942, 1942a; Morgan, 1930; Pierre and Scarseth, 1931; Reed *et al.*, 1939; Ross *et al.*, 1964; and Shaw, 1952). Such efforts have been, at best, only partially successful, particularly if one attempts to estimate precise levels of base saturation from pH measurements. For example, Shaw working with New York soils (surface and subsurface horizons) plotted pH in water and $CaCl_2$ versus base-saturation percentage and found that, for any given base-saturation level, the actual pH may vary ± 0.5 pH units. Pierre and Scarseth conclude that soils of similar origin and degree of weathering may differ by 20% in their base-saturation percentage at like pH values. Inferences of base saturation from pH, as estimated with filed pH kits, are even more hazardous, because such estimates are usually not closer than a few tenths to the absolute value. This disparity could be significant particularly as one approaches a pH limit used to infer a specific base-saturation level.

The purpose of this study is to evaluate the utility of employing pH in water and in KCl solutions to infer base status of samples of surface and subsoil horizons collected from various great soil groups extensive in Ohio. The advantage, if any, of using pH measured in 1 *N* KCl to make more accurate predictions is also considered.

MATERIALS AND METHODS

Sixty-four soils representing three soil orders were selected for study (fig. 1); 17 were Mollisols or Mollic Intergrades (Humic Gleys), 28 were Alfisols (Gray-Brown Podzolics), and 19 were Ultisols or Ultic Intergrades (Red-Yellow Podzolics). These are soils of major extent in Ohio that vary widely in their physical, chemical, and mineralogical properties. Three horizons (Ap, B1, and B2, or equivalents) of each soil were analyzed to evaluate the integrated effect of organic matter and

clay on pH and base-saturation relationships. All chemical and physical data presented, except pH, were previously obtained by the Soil Characterization Laboratory at The Ohio State University for soil profiles collected in conjunction with the Ohio Soil Survey program. (The critical horizons for determining classification between Alfisols and Ultisols were not employed in this work because samples were not available to a depth of 50 inches below the top of the argillic horizon.)

Particle-size distribution for these soils was determined by using the sedimentation-pipette method of Steele and Bradfield (1934), modified by using sodium hexametaphosphate as the dispersing agent. Percentage of fine clay (<.2u) was determined by a centrifugation-pipette procedure. Exchangeable calcium and

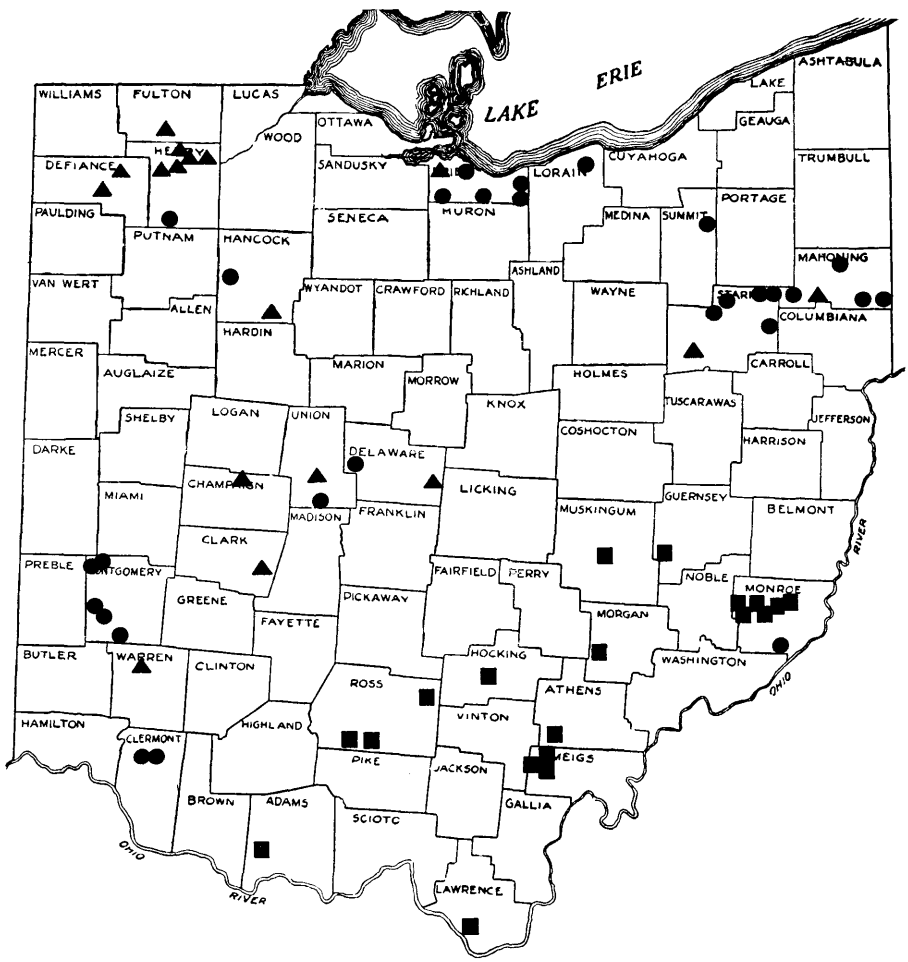

FIGURE 1. Location and distribution of profiles investigated in Ohio.

magnesium were determined by the Barrows and Simpson method (1962) using 1 N NH_4OAc buffered to pH 7.0. The extract was then analyzed for exchangeable potassium on a Beckman DU Spectrophotometer at 770 mμ. Total acidity was determined by the Mehlich buffer method (1962) using barium chloride buffered with triethanolamine to pH 8.2. Cation-exchange capacity was attained by the summation of exchangeable Ca^{++}, Mg^{++}, K^+, and H^+. Free salts and other exchangeable cations are negligible in these soils. Percentage organic matter was measured by the Walkley-Black method (1934) of wet digestion with chromic acid. Soil pH measurements were made as follows:

(a) *1:1 (soil: water)*—10 ml distilled water were added to a 10-g air-dried soil sample (<2mm). The sample was then stirred to form a paste, allowed to set for 1 hour, restirred, and the glass pH electrodes immediately immersed in the suspension. Using a Beckman Model G pH meter, pH was measured within 10–15 seconds after immersion of electrodes into the suspension.

(b) *1:2 (soil: 1N KCl)*—10 ml of 2N KCl solution were added to the 1:1 soil-water suspension (yielding 1N KCl) and subsequently handled as described above. The change in pH ($\triangle$ pH) was calculated as the difference between pH in water and pH in KCl.

Data were stratified by soil order and horizon prior to computing the following simple linear regression relationships:

(a) pH in KCl as a function of pH in water;
(b) Base-saturation percentage as a function of:
  1) pH in water,
  2) pH in KCl,
  3) pH in water expressed as hydrogen-ion concentration [H^+],
  4) pH in KCl expressed as hydrogen-ion concentration [H^+].

RESULTS AND DISCUSSION

Soil Characteristics

Means, ranges, and standard deviations of selected physical and chemical properties for soils used in this study are listed in Table 1. Mollisols and Mollic-intergrades represent the more youthful soils from the standpoint of profile development and intensity of weathering. These poorly drained soils are characterized by high base-status, high organic-matter contents, and increasing pH with depth. A weak argillic horizon is present in some soils studied, but absent in others. Relatively high cation-exchange capacities are attributed to higher organic-matter contents, higher clay contents, and to their montmorillonite- (or vermiculite-) rich clay mineralogy. This is particularly true for those soils derived from the strongly calcareous glacial deposits of western Ohio. Soils of the Lake-Plain Region, on the other hand, are dominantly illitic, with secondary quantities of vermiculite.

Alfisols in general are intermediate in degree of profile development and weathering between Mollisols and Ultisols. Argillic horizons are characteristic of both the Alfisols and Ultisols, and vary in degree of expression from weak to moderate, as suggested from increases in clay content from surface to subsoil horizons. Base saturation of Alfisols is diagnostically higher than for Ultisols, as discussed previously. Alfisols and Ultisols generally have lower organic matter contents, pH, and base saturations throughout the entire profile than do Mollisols. In general, lower cation-exchange capacities in the Alfisols and Ultisols reflect their lower organic-matter contents, lower clay contents, and clay mineralogy. Illite, vermiculite, and interstratified mixtures of these two components represent the major clay minerals in these soils. The more strongly weathered A and upper

TABLE 1

Statistical summarization of selected soil chemical and physical properties

Horizon	Statistic	Depth (inches)		Clay		Organic matter	Base Sat.	CEC (meq/-100g soil)	Total acidity (meq/-100g soil)	pH		
				Total %<2 μ	Fine %<.2 μ	%	%			1:1 H_2O	1N KCl	△pH
						Mollisols and Mollic Intergrades						
Ap	Mean	0*	8†	35.0	14.1	5.1	73	33.4	8.8	6.1	5.3	.8
	Range	—	5–	8.5–	2.9–	2.9–	47–	15.5–	3.3–	5.1–	4.2–	.7–
			10	54.0	21.2	7.5	87	46.7	19.5	7.2	6.1	1.0
	SD	—	1	13.6	5.7	1.7	11	7.4	4.1	.6	.6	.1
	N	13	13	14	14	14	14	13	13	14	14	14
B1	Mean	9	15	40.3	17.9	1.9	80	26.6	5.1	6.5	5.5	1.0
	Range	6	9–	10.9–	4.8–	.7–	55–	10.2–	2.0–	5.3–	4.3–	.6–
		13	19	68.2	31.8	4.0	91	37.9	11.9	7.2	6.3	1.3
	SD	2	3	14.4	6.6	1.0	9	8.3	2.6	.6	.6	.2
	N	17	17	17	17	17	17	17	17	17	17	17
B2	Mean	15	22	41.0	18.6	1.3	84	25.7	4.1	6.7	5.6	1.1
	Range	12–	15–	16.6–	8.9–	.6–	69–	14.8–	2.0–	5.9–	4.9–	.7–
		19	27	77.1	34.9	2.3	91	35.4	7.3	7.4	6.3	1.5
	SD	2	3	16.1	7.2	6	6	5.9	1.7	.5	.4	.2
	N	14	14	14	14	14	14	14	14	14	14	14
						Alfisols						
Ap	Mean	0	8	16.6	4.1	2.6	58	15.1	6.3	6.0	5.1	.9
	Range	—	5–	5.5–	.5–	1.4–	12–	8.0	2.4–	4.4–	3.5–	.6–
		—	10	27.2	10.7	3.8	85	20.5	16.0	6.9	6.3	1.2
	SD	—	1	5.0	2.1	.8	18	3.0	3.3	.7	.7	.1
	N	28	28	28	28	28	28	28	28	28	28	28
B1	Mean	9	14	24.4	8.6	.8	49	15.3	7.8	5.3	4.1	1.2
	Range	5–	9–	3.0–	.3–	.3–	20–	4.4–	2.1–	4.4–	3.2–	.9
		21	27	51.8	24.7	2.4	77	27.9	22.4	6.6	5.5	1.4
	SD	3	4	11.1	5.7	.5	16	5.7	4.7	.7	.7	.2
	N	28	28	28	28	28	28	28	28	28	28	28
B2	Mean	13	20	31.3	13.7	.6	51	19.4	9.7	5.1	4.0	1.1
	Range	9–	11–	3.6	1.3–	.2–	25–	4.3–	1.5–	4.4–	3.1–	.9
		27	48	60.8	31.9	1.1	86	34.6	25.9	6.9	6.0	1.4
	SD	4	8	14.3	8.0	.3	19	7.7	5.6	.7	.8	.2
	N	27	27	27	27	27	27	27	27	27	27	27
						Ultisols and Ultic Intergrades						
Ap	Mean	0	6	18.1	4.1	2.7	47	14.9	7.8	5.5	4.6	.9
	Range	—	3–	12.5–	2.1–	1.5–	8–	8.7–	2.7–	4.4–	3.6–	.6–
		—	9	25.5	8.5	6.8	80	22.4	13.9	6.9	6.3	1.6
	SD	—	2	3.7	1.4	1.1	20	3.0	3.2	.8	.9	.2
	N	19	19	19	19	19	19	19	19	19	19	19
B1	Mean	9	13	26.9	9.7	.7	35	15.8	10.1	4.9	3.7	1.2
	Range	6–	9–	14.6–	4.0–	.3–	11–	8.7–	4.3–	4.6–	3.5–	.9–
		16	21	36.4	18.5	1.3	62	25.3	14.8	6.1	4.9	1.3
	SD	3	4	6.4	4.4	.3	13	4.5	3.0	.4	.4	.1
	N	15	15	15	15	15	15	15	15	15	15	15
B2	Mean	14	18	28.5	12.0	.4	36	16.6	10.8	4.9	3.8	1.1
	Range	9–	15–	16.1–	2.8–	.1–	16–	10.1–	3.9–	4.6–	3.5–	1.0–
		21	24	39.0	22.6	.9	72	21.9	16.9	6.0	4.9	1.2
	SD	3	3	7.1	5.0	.2	17	4.0	3.8	.4	.4	.1
	N	11	11	11	11	11	11	11	11	11	11	11

*Upper horizon boundary.
†Lower horizon boundary.

B horizons, especially in Ultisols, characteristically contain substantial quantities of hydroxy-aluminum interlayered between vermiculite (and occasionally montmorillonite) clay lattices, forming chloritized specimens. Such interlayers block active exchange sites and effectively lower the exchange capacity of such highly charged clays.

Correlation of pH in Water with pH in KCl

Values of soil pH determined in water versus those determined in KCl solution are closely correlated and yield r values (correlation coefficients) ranging from 0.897 to 0.984 (figs. 2–4). For the soils studied, the pH measured in KCl is

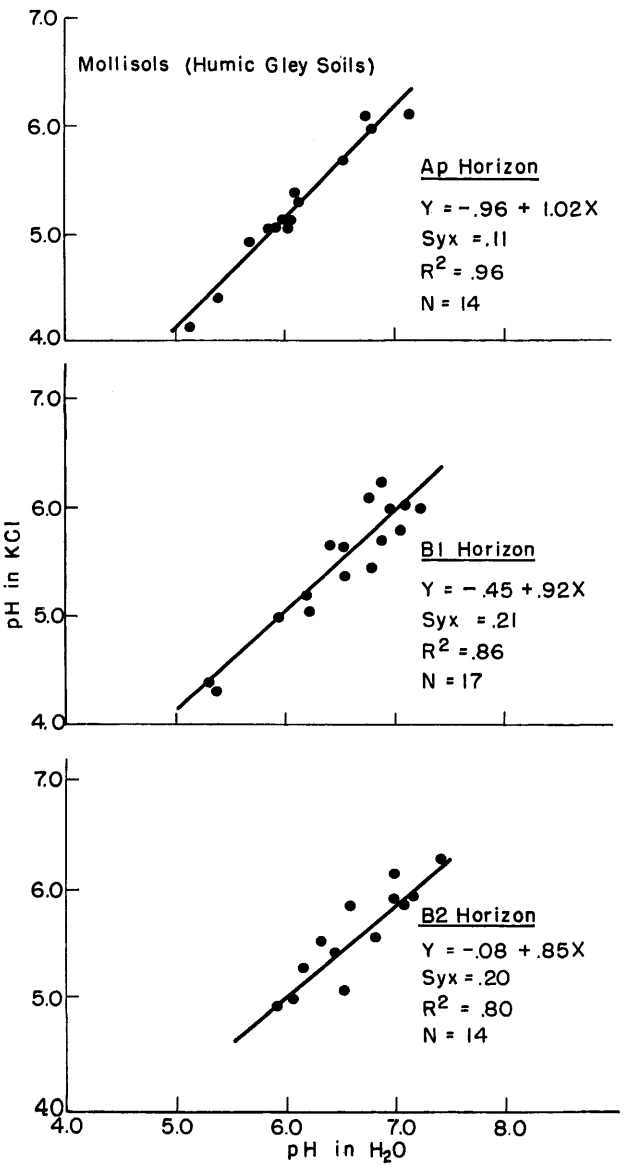

FIGURE 2. Regression relationship between pH in water and KCl for Mollisols.

approximately one unit lower than is the pH in water (Table 1). The difference in pH as measured in KCl versus pH in water (△pH) tends to be minimum in surficial horizons and to reach a maximum in lower subsoil horizons. For Ohio soils, if the pH in water is known, the pH in KCl can be predicted to within 0.2 or 0.3 of a pH unit at the 95% confidence level, using regression relationships as given in Figures 2–4. Keeney and Corey (1963), working with the Ap horizons of twenty-six Wisconsin soils, also found that pH as measured in water was approximately one unit higher than pH in KCl. This difference was consistent for all soils they studied.

Although in this study, values obtained for △pH were similar for A and B

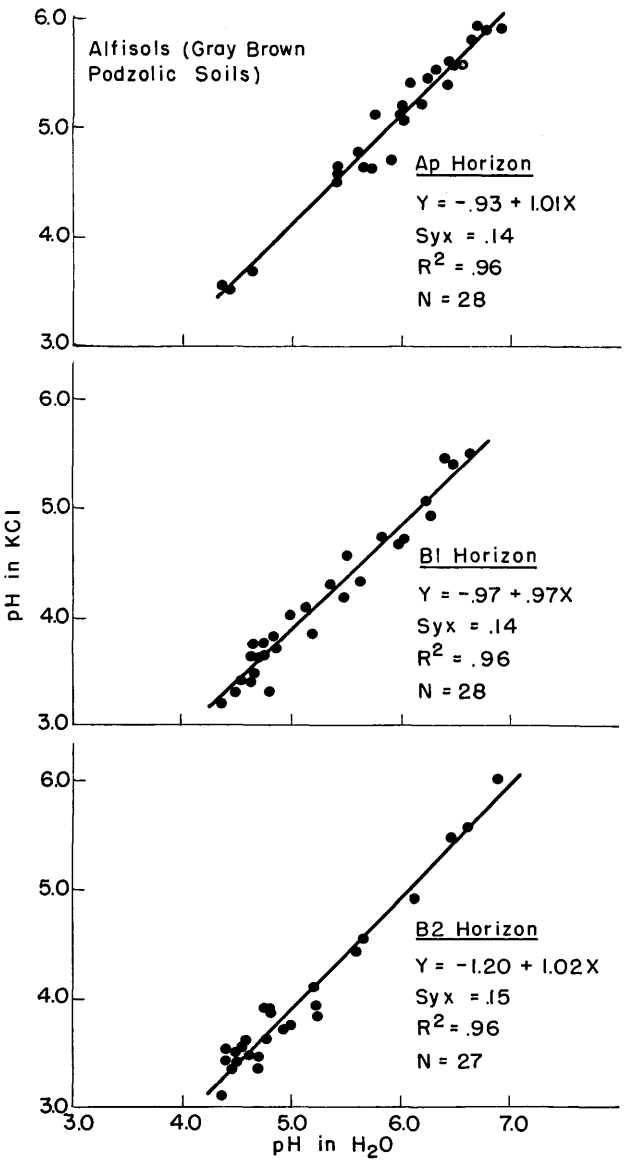

FIGURE 3. Regression relationship between pH in water and KCl for Alfisols.

horizons of all three soil orders (Table 1), the proportion of total acidity (exchangeable acidity) that becomes active with addition of KCl to aqueous suspensions is not constant. This is because pH is a logarithmic function, and thus, to determine the proportion of total acidity that is active, pH values must be converted to hydrogen-ion concentrations [H^+], and taken as the ratio of total acidity, expressed as [H^+]. This difference in active acidity is equal to:

$$\frac{[H^+]_{KCl} - [H^+]_{H_2O}}{\text{Total acidity } [H^+]}.$$

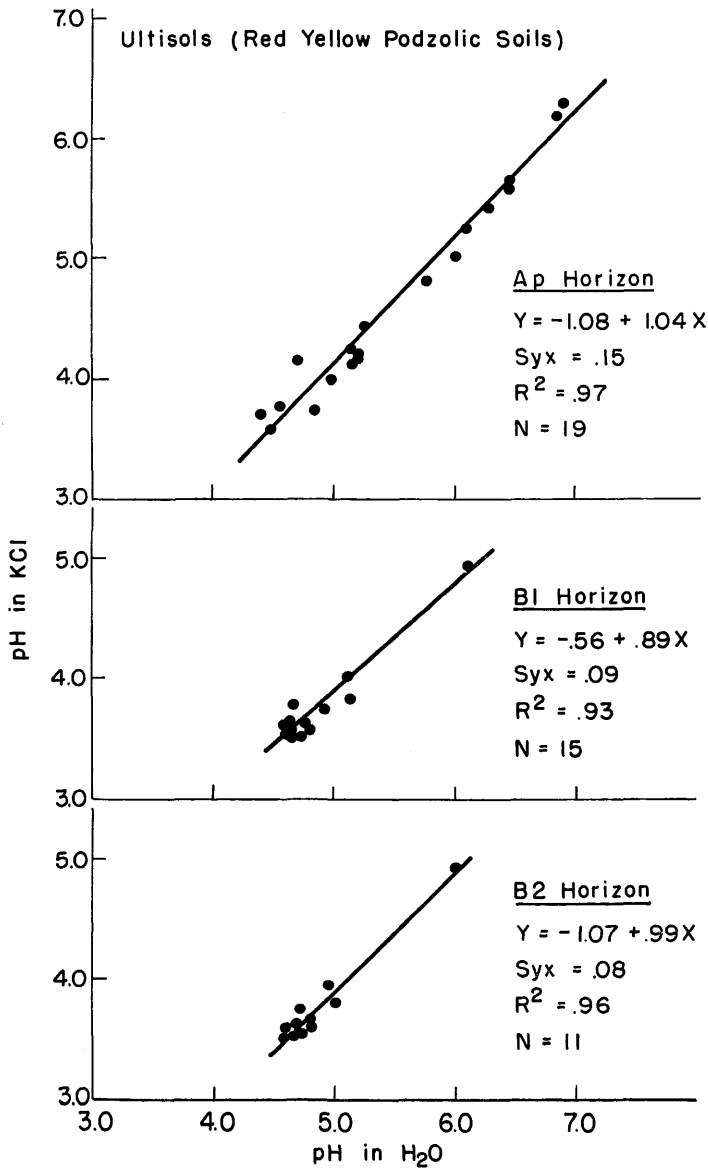

FIGURE 4. Regression relationship between pH in water and KCl for Ultisols.

Following are the results for each soil order and horizon expressed in moles/liter/10 g soil times 10^{-4}:

Horizon	Mollisols	Alfisols	Ultisols
Ap	0.92	3.00	6.35
B1	1.13	15.54	19.53
B2	0.78	20.13	15.61

Larger amounts of total acidity become active in KCl suspensions for Alfisols and Ultisols than for Mollisols. The proportion of total acidity that becomes active in KCl increases with depth in the Alfisols and Ultisols, but remains nearly constant in the Mollisols. This difference may be explained by the nature of cation-exchange sites (pH-dependent versus permanent) as governed by organic-matter content, pH, and clay mineralogy.

That portion of the cation-exchange capacity which is of permanent charge is defined as the net negative (or positive) charge of clay particles inherent in the crystal lattice of the particle, and is not affected by changes in pH or ion-exchange reactions. The permanent charge reflects differences in charge densities among clay-mineral species. On the other hand, pH-dependent charge is defined as that portion of the total charge of the soil particles which is affected by, and varies with, changes in pH. Organic matter is a source of strong pH-dependent charge in soils and, as pH increases, the cation-exchange capacity of this component increases exponentially. Ap and upper B horizons of Mollisols with relatively high organic-matter contents and high pH's tend to dominate the montmorillonite-rich clay mineralogy and thus would be expected to have a cation-exchange capacity that is strongly pH-dependent. According to Snyder *et al.* (1969), such sites would favor a lower release of H^+ by K^+, because H^+ is more strongly bonded to pH-dependent sites than are other cations subject to displacement by K^+.

In Ap horizons of Alfisols and Ultisols, a mechanism similar to that in the Ap horizon of the Mollisols may be operative. However, in the B1 and B2 horizons of these soils, mean pH values and organic-matter contents decrease sharply (Table 1) relative to their values in the A horizons. Thus with little organic matter, more of the exchange capacity of the illitic, vermiculitic, and interstratified clay minerals present would reflect permanent charge sites. It is well established that K^+ is more strongly bonded to permanent charge sites than to pH-dependent charges Snyder *et al.* (1969); thus a greater proportion of the total acidity would be expected to be displaced into solution with addition of KCl in these horizons.

Correlation of Base-Saturation Percentage with pH

Correlation of base-saturation percentage with pH in water and KCl yielded simple correlation coefficients (r) ranging from 0.596 to 0.928 (Table 2). In all cases these relationships were highest for A1 and lowest for B horizons. The relationship between base-saturation percentage and pH in water was generally more closely associated than was base-saturation percentage as a function of pH in KCl, or pH expressed as hydrogen-ion concentration for these two systems (Table 2). Base-saturation percentage was also correlated with ratios of pH in water or KCl to total acidity (expressed as hydrogen-ion concentration), but such simple correlations were improved only slightly for the Ap and B1 horizons of Mollisols and were unchanged or lower for the Alfisols and Ultisols (data not presented). For this reason, and because no evident advantages could be detected for using alternate relationships of pH in KCl or ratios of active to total acidity to estimate base saturation, the following discussion will center on simply utilizing pH in water to infer soil base-saturation percentage.

In Mollisols, correlation coefficients for pH in water versus base-saturation

percentage decreased as follows: r=0.838 in Ap, 0.740 in B1, and 0.682 in B2 horizons. This suggests that pH in water accounted for about 46 to 70% of the total variability in base-saturation percentage. Similar trends were obtained

TABLE 2

Simple correlation coefficients (r) for the regression of soil base saturation on pH (as expressed in both logarithmic and [H^+] values) for water and 1N KCl suspensions

Soil order	pH suspension	Base saturation as a function of: pH			pH expressed as [H^+]		
		Horizon			Horizon		
		Ap	B1	B2	Ap	B1	B2
Mollisol	Water	0.838	0.740	0.682	0.875	0.827	0.700
	KCl	0.847	0.687	0.704	0.854	0.784	0.763
Alfisol	Water	0.892	0.773	0.726	0.772	0.727	0.732
	KCl	0.887	0.724	0.687	0.625	0.460	0.347
Ultisol	Water	0.928	0.668	0.801	0.804	0.639	0.531
	KCl	0.909	0.596	0.785	0.597	0.502	0.462

for Alfisols and Ultisols. Scatter diagrams and best-fit regression equations for these two parameters are presented in Figures 5–7.

Base saturation percentage of Ap horizons for all three soil orders can be predicted to within 6 to 8% of the observed values from pH data 68% of the time (figs. 5–7). All of the Mollisol, 91% of the Alfisol, and 86% of the Ultisol Ap horizons with pH values of 5.5 or more have base saturations of 50% or greater. Of those Ap horizons with a pH of less than 5.5, 83% of the Alfisols and 91% of the Ultisols have a base status of less than 50% (Table 1 and figs. 5–7). On this basis, a pH of 5.5 could be selected to differentiate mollic from umbric epipedons (base saturations above versus below 50%) and be correct over 90% of the time.

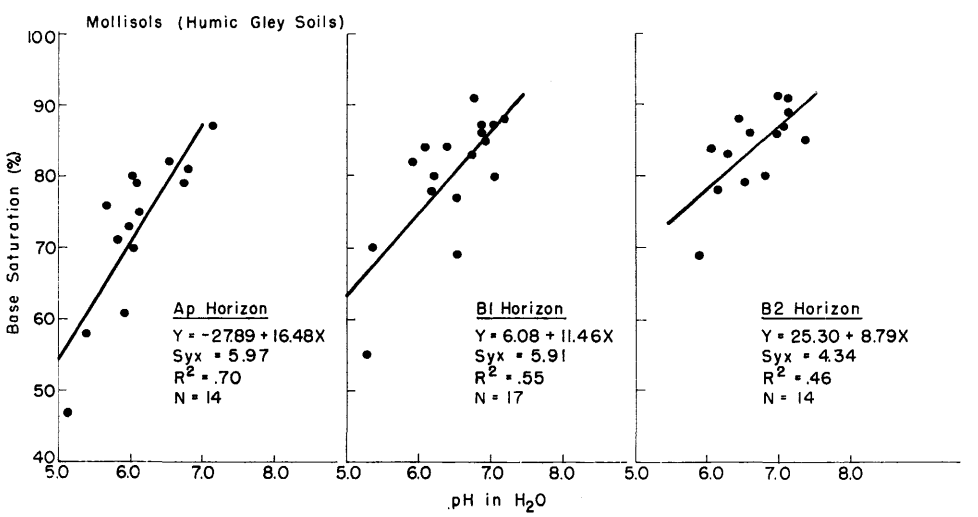

FIGURE 5. Regression relationships between base saturation and pH in water for A and B horizons of Mollisols.

In contrast, the ability to estimate base saturation from pH data for subsoi-horizons is much less reliable than for surficial horizons. This problem is pars ticularly acute for Alfisols and Ultisols, where the utility of such estimates is necessary to differentiate between these two soil orders. In B1 and B2 horizonl of these soils, observed base-saturation percentages can be expected to vary as much as 9 to 14% from the calculated values 68% of the time, and 18 to 28% in 95% of the cases (figs. 5–7). In estimating whether the base-saturation percentage is above or below 35%, the most critical pH region is between 4.5 and 5.0. In

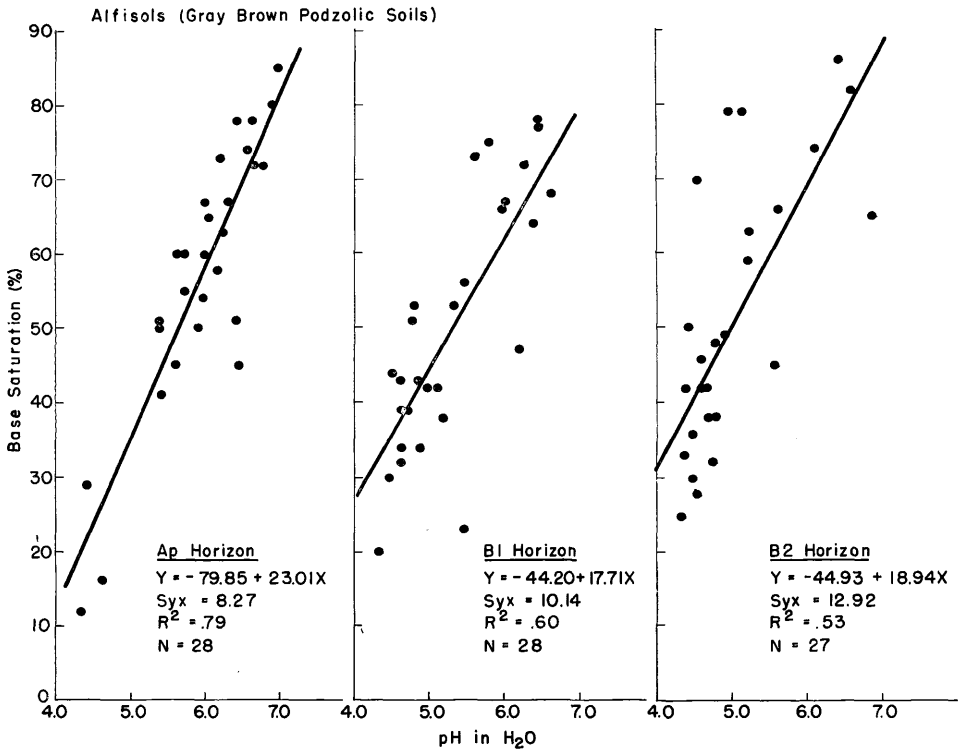

FIGURE 6. Regression relationships between base saturation and pH in water for A and B horizons of Alfisols.

this range, base-saturation percentages vary from 20 to 80% with little tendency to co-vary with pH. With few exceptions, subsoil horizons of Alfisols and Ultisols with pH values of 5.0 or above have base-saturation percentages above 35%. For Alfisols, approximately two-thirds of the subsoil horizons with a pH of between 4.5 and 5.0 have a base-saturation percentage greater than 35%, while the converse is true for horizons with a pH of less than 4.5. In Ultisols, approximately one-half of the horizons with a pH of 4.5 to 5 have base-saturation percentages above 35% and half below this level. Thus, a pH value of 5.0 or above could be used with a relatively high degree of reliability to differentiate those soils with a base status above 35%. Unfortunately, as one approaches the 35% base-status limit, most of the observations have pH's which fall between the values of 4.5 and 5.0. This is related to the chemistry of hydroxy-aluminum interlayers between clays, and corresponds to the critical pH range for formation and hydrolysis of this com-

ponent (Rich, 1960). In this situation, little confidence can be placed on the estimate of base saturation from field or laboratory pH data. At this time, the only recourse is to determine the base-saturation percentage of such soils directly in the laboratory. If such a differentiating criterion is to be an operational class definition applicable under field conditions, increasing attention must be given to a relatively rapid, accurate method to determine this parameter in the field.

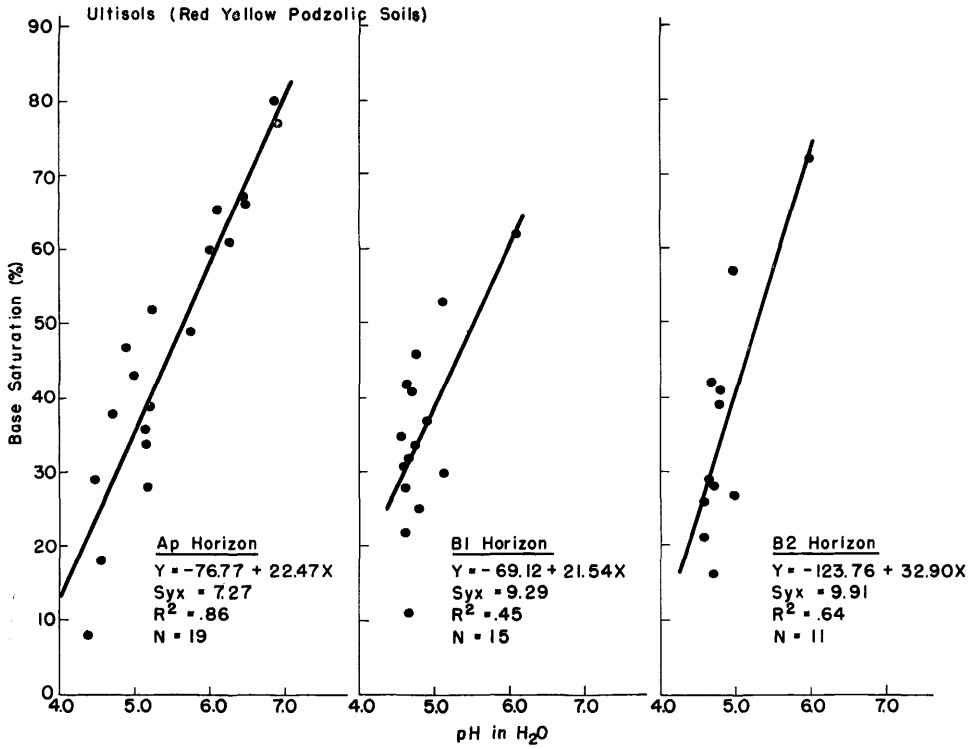

FIGURE 7. Regression relationships between base saturation and pH in water for A and B horizons of Ultisols.

SUMMARY

From this study, it may be concluded that, for Ohio soils:

(a) There seems to be little advantage in measuring soil pH both in water and in KCl. The pH in the latter can be accurately predicted for these soils to within 0.2 to 0.3 of a unit from regression equations presented. It is usually about one unit lower than the pH in water.

(b) Soil pH determined in water is equal to or better than pH determined in KCl, active acidity in water or KCl (expressed as hydrogen-ion concentration), or the ratio of active acidity in water or KCl to total acidity as an indicator of base-saturation percentage.

(c) Base-saturation percentage can be estimated from pH in water with greater reliability in surface horizons than in subsoil horizons for Mollisols, Alfisols, and Ultisols. This implies that pH may be a useful tool in differentiating mollic from umbric epipedons, but becomes of increasingly limited use in separating Alfisols from Ultisols as one approaches the base-saturation percentage class limit defining these two orders.

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